DECOMPOSITION KINETICS OF THE
ROCKET OXIDIZER AMMONIUM PERCHLORATE

BY

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ABSTRACT

The effect of catalysts on the deflagration pressure-limit and the burning rate of ammonium perchlorate was studied. The catalysts used were copper chromite, ferric oxide, cupric oxide and potassium permanganate.

Copper chromite, Fe_2O_3 and CuO increased the lower pressure limit of deflagration when present at small concentrations and decreased it at large concentrations. Potassium permanganate, both mechanically mixed and co-crystallized with ammonium perchlorate, had a similar effect on the lower pressure limit. However, at large concentrations of $KMnO_4$, an upper pressure limit was observed above which deflagration could not be maintained. Catalysts were much more effective at smaller particle sizes.

The effect of these catalysts on the burning rate was a function of the pressure. This effect became significant at high pressures especially in the range above 2000 psi where the burning rate of pure ammonium perchlorate goes through a minimum.

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CHAPTER I

INTRODUCTION

Ammonium perchlorate (NH_4ClO_4, denoted herein as AP), like several other perchlorates, has long been of chemical interest as an oxidizer and has found technological application in explosives, pyrotechnics, and propellants. Since 1940, however, increasing use has been found for AP as an oxidizer in composite propellants.

Composite propellants are one type of solid propellants in which an oxygen-containing inorganic salt such as ammonium perchlorate, potassium perchlorate, ammonium nitrate, nitronium perchlorate, nitrosyl perchlorate, hydrazine perchlorate, hydroxylamine perchlorate or hydrazine diperchlorate is dispersed in a suitable matrix or "binder" of a polymeric fuel such as polyurethane or polyisobutylene. Small quantities of catalysts and other chemicals are also added to modify the burning characteristics.

Solid propellants undergo a self-sustained steady combustion (deflagration), if the pressure of the surrounding gas is above a critical pressure which is usually called the low-pressure deflagration limit or simply the low pressure limit. The deflagration process is an interaction of many physical and chemical changes in the oxidizer and the fuel. This process is very complex due to the heterogeneity of the solid phase and also due to the occurrence of a large number of rapid changes

in very thin zones in the vicinity of the phase
boundaries. s'ice it is difficult to reveal the nature
of these changes by studying the deflagration of actual
composite propellants, most of the fundamental studies
have been on the systems which have a much simpler
structure than the actual propellants.

One area of such fundamental investigations has
been the study of decomposition and combustion of pure
AP, which is the most commonly used oxidizer. The
literature in this area is very extensive and has been
reviewed several times (30,43,48,59). Such studies are
important because the combustion of AP plays an important
role in the combustion of AP-based propellants. Also,
since AP deflagrates as a monopropellant, it can be used
as a relatively simple system for studies on the
fundame. .' .s of deflagration.

 noni'm perchlorate is stable at room temperature
and atmospheric pressure but decomposes at measurable
rates at temperatures above 150°C. At temperatures
below approximately 300°C, AP undergoes an autocatalytic
reaction which ceases after about 30% decomposition.
This is usually called the low-temperature decomposi-
tion. The residue is quite stable at these temperatures
unless rejuvenated by sublimation, recrystallization,
or mechanical disturbance (5,6,7,25). At temperatures

between 350 to 450°C, the high-temperature decomposition occurs; this reaction is not autocatalytic and goes to completion. Concurrently with these decomposition reactions, AP undergoes dissociative sublimation (5,6,25). At temperatures above 440 to 450°C, the thermal decomposition is very fast and is usually referred to as thermal explosion (6).

The mechanism of the decomposition reactions is not definitely known. Proton transfer, electron transfer, and decomposition of the anion are the most commonly suggested mechanisms (6,7). However, there are strong indications that the low-temperature decomposition and the sublimation of AP are by proton transfer.

The effects of a wide variety of additives on the thermal decomposition of AP have been studied (5,6,7,26, 33,37,40,42,48,66,68,69,79,80,83-87). Some of the effective decomposition catalysts are copper oxides, copper chlorides, ZnO, NiO, Cr_2O_3, MnO_2, MgO and cobalt oxides. Usually, p-type catalysts are more effective than n-type with some exceptions such as ZnO (47).

The combustion of AP also has been studied extensively. Originally, it was thought that decomposition and combustion of AP were basically similar and understanding one could help to understand the other one. Later, experimental progress in both fields showed that the kinetics and mechanism of these two processes were quite different. Thus the available data on the decomposition of AP could not be extended to the deflagration

conditions. Therefore, gradually more research effort was directed towards the study of the combustion rather than the decomposition of AP.

The most important parameter of AP combustion is the linear burning rate. The effects of pressure, AP particle size, strand density, ambient temperature, and catalytic additives on the burning rate have been studied (10,15,22-24,27,28,51,74,76,91,93). The principal interest has been the pressure dependence of the burning rate. A collection of the representative data on this subject is shown in Fig. I-1. There is a general agreement among the data up to about 2000 psi. At higher pressures, however, the data are scattered, but mainly fall in two categories: one category shows a further increase in the burning rate with pressure; the other one indicates a sharp decrease and a minimum in the burning rate around 4000 psi. The reason for such scattering and the sharp drop in the burning rate, observed by some investigators, has been the subject of many discussions. Recently, it was found that the main reason for the scattering of data in this pressure range is the effect of impurities (15,72). Also, it was shown that the dip in the burning-rate curve is a natural attribute of AP deflagration (14,15). However, the reason for such phenomena is not yet clearly known.

The other measured parameter in the combustion of AP is the deflagration limit. It has been known that

Figure I-1.   Burning rates of ammonium perchlorate at room temperature in an inert atmosphere.

AP undergoes a self-sustained combustion at pressures higher than a lower pressure limit. This limit is 300 psi at 20°C and changes with the solid temperature, AP grain size and addition of catalysts (24,27,28,50, 51,64,92). The existence of such a pressure limit has been pondered at length and has remained without a satisfactory explanation.

The theoretical modeling of the deflagration and the ignition of AP and propellants in general is another aspect of the combustion studies which has received considerable attention. Despite extensive research in this area, the existing models cannot predict and explain the most elementary of the basic experimental observations: the ignition point and the low pressure limit. A successful theoretical modeling requires some precise knowledge of the mechanism and the kinetics of the steps involved in the combustion. Unfortunately, very little is known in this respect, mostly because of the experimental difficulties. Most of the existing experimental data are on the overall characteristics of burning such as the burning rate, the deflagration limit, and the composition and temperature of the final products. Such studies bypass the mechanism and kinetics of the intermediate processes.

Recently, there have been some attempts to under-stand the nature of the intermediate steps. The most

fruitful investigations of this type have been the studies of the characteristics of the burning surface (the surface boundary between the gaseous and the condensed phase).

One important surface parameter is the surface temperature. Different techniques have been used to measure this temperature. In the early studies, fine thermocouples embedded in AP-strands were used (9,67). This technique is not very reliable because the size of the junction of a very fine thermocouple is still comparable to the depth of the reaction zone; therefore, thermocouples measure some average temperature in such a zone which has a very steep temperature gradient.

Powling et al. (62,63) used an infrared-emission method. Their technique was fairly reproducible at low pressures and low burning rates. However, the measurements became erratic at pressures above 60 psi due to the interference of the gaseous products covering the surface. A modification of this technique was employed by Selznev et al. (70). They measured the radiation from the surface by inserting a light guide in the AP strands.

A third technique used for measuring the surface temperature is based on the crystallographic transition which takes place in AP at 240°C. Selzer (71) and Beckstead et al. (4) measured the thickness of the

transition zone where AP has a cubic crystal structure and, from the knowledge of the burning rate, calculated the surface temperature.

In general, the results obtained by the above methods do not agree. Any of these techniques suffer short-comings and cannot be completely relied upon. The accuracy of these measurements is especially subject to doubt in the light of the new information about the existence of a frothy melt on the solid surface (35).

Recently, there have been some studies on the detailed structure of the burning surface. High-speed movies of the burning surface and the scanning electron microscope micrographs of the quenched samples have revealed some important features of the burning surface and the reaction zone. Hightower and Price (35), for the first time, reported the existence of a melt on the surface of the burning AP crystals. Boggs et al. (10,12,13) made a more thorough investigation over a wide range of combustion pressure and confirmed the existence of a frothy melt. They found that the thickness of the melt decreased with pressure. At pressures above 900 psi the surface was partially dry and at pressures above 2000 psi, where the burning rate goes through a minimum, the surface was covered by a layer of needle-like crystallites.

An important aspect of the combustion of AP which requires more experimental study is the role of catalysts in the deflagration process. Even though addition of catalysts introduces new complications to an already unsolved problem, it can provide very useful and necessary information for the following reasons: First of all, the sensitivity of the combustion of AP to traces of catalytic impurities is an important source of the disagreement among the existing data. Therefore, it is essential to know this catalytic effect in order to explain the present discrepancies. Secondly, such data could be an indirect way of obtaining more insight into the deflagration reactions. In other words, the effect of catalysts on the combustion parameters could be used to test the validity of some basic assumptions in the theoretical modeling and probably would give some clues to the mechanism of the steps which cannot be isolated and studied separately. Finally, the data in this field have a great practical importance because catalysts are actually used in propellants to increase the combustion rates.

The present work was mainly devoted to the study of the role of catalysts in the deflagration of AP. The experimental aspect of this work dealt with the effects of catalysts on two important deflagration parameters: the deflagration limits and the burning rate of AP.

The remainder of this report is devoted to the discussion of the effects of catalysts on the deflagration limits and burning rate of AP. Three appendices follow which give specifications of "as received" AP, experimental apparatus, and the experimental data.

CHAPTER II

THE EFFECT OF CATALYSTS ON THE DEFLAGRATION LIMITS

OF AMMONIUM PERCHLORATE

INTRODUCTION

Ammonium perchlorate undergoes self-sustained combustion (deflagration) only in certain pressure ranges, giving rise to pressure limits. The lowest pressure at which deflagration can be maintained is called the lower pressure limit or the lower deflagration limit. Similarly, the highest pressure for deflagration is called the upper pressure limit.

Of these two limits, the lower pressure limit has greater practical importance and has been the subject of many theoretical and experimental studies. Even though there is no satisfactory model which can explain and predict the lower pressure limit, a value of 300 psi at 21°C for pure AP (single crystals or polycrystalline pellets) is almost universally accepted from experiments. By contrast, the upper pressure limit has not been systematically studied; in fact, even its existence is not fully accepted and agreed upon.

Friedman et al. (24) first reported the existence of an upper pressure limit of 200-300 atm (depending on the particle size) at 21°C. They also reported a lower pressure limit of 45 atm under these conditions. However, later studies by Levy and Friedman (50) and other investigators showed that this value of the lower

pressure limit was too high, most probably due to the use of a weak ignition source. The lower pressure limit was then corrected and extended to a much lower value of 22 atm which was reported to be independent of the ignition flux. Levy and Friedman (50) also showed that the upper pressure limit previously observed was eliminated when the pellets were wrapped in an asbestos shield. The logical consequence of this observation to them was that the upper pressure limit is due to some convective heat losses which become important at high pressures.

Later studies (9,27) showed that at high pressures there is a sudden significant decrease in the burning rate, but the deflagration can be maintained without insulating the samples even up to pressures as high as 10,000 psi.

In addition to the lower pressure limit and the upper pressure limit, there are two cases reported where deflagration could not be maintained at a certain pressure range. The first case was observed by Watt (91). In his study of the effect of solid temperature on the deflagration rate, he noticed that at -28°C deflagration could not be easily maintained between 600 and 2000 psi. However, due to limited experimental data he did not conclude that deflagration was impossible in this range. A similar case was reported by Boggs et al. (14) in the deflagration of doped AP containing 0.0083 and

0.015 wt-% $Cr_2O_7^{--}$. The location and width of the non-burning pressure range in this case depended on the concentration of dichromate in AP.

The pressure limits can be very sensitive to catalysts. Friedman et al. (24) observed that 3 wt-% of Pt black, copper chromite, CuO, Cr_2O_3, Fe_2O_3, MnO_2, or $NaMnO_4 \cdot 3H_2O$ increase the lower pressure limit of AP considerably and eliminated the upper pressure limit at least up to 340 atm, which was their maximum operating pressure. Since copper chromite is one of the most effective catalysts for deflagration of AP, they studied its effect in greater detail and found that small additions of copper chromite raised the lower pressure limit and large additions lowered it. The maximum lower pressure limit was about 170 atm, corresponding to 0.3 wt-% of copper chromite. The decrease in the lower pressure limit at high concentrations of catalysts is also reported by Shidlovskii et al. (77,79), Bakhman et al. (30), and Powling (61). The data on the change in the deflagration limit with addition of catalysts are summarized in Table II-1.

Except for some very qualitative explanations, no satisfactory model exists yet to explain the above experimental observations regarding the effect of catalysts on the pressure limits. This is understandable when one considers that the lower pressure limit itself is not very well understood and the mechanism of combustion in the very thin reaction zone is not satisfactorily known.

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Table II-1

THE EFFECT OF CATALYSTS ON THE LOWER PRESSURE LIMITS OF AP

Authors and References	Catalyst Nature	Catalyst Concentration (wt %)	Ambient Temperature[a] °C	Density gm/cc	Lower Pressure Limit (atm)
Levy and Friedman (50)	copper chromite	0.0001		1.8 -1.9	22
		0.001		1.8 -1.9	25
		0.01		1.8 -1.9	110
		0.1		1.8 -1.9	160
		1.0		1.8 -1.9	140
		3.0		1.8 -1.9	40
		10.0		1.8 -1.9	15
		50			<1
		75			75
	Pt black	0.025			120
	MnO_2	3			140
	$NaMnO_4, 3H_2O$	3			90
	Fe_2O_3	3			65
	Cr_2O_3	3			220
	CuO	3			140
	CaO	1			340
	$CaCO_3$	1			340
Powling (61)	$CnCo_3$	3			<1
Shidlovskii et al. (77)	Cu_2Cl_2	0.5			<1
	$Cu_2Cl_2, 2H_2O$	2			<1
	MnO_2	5			<1
	$KMnO_4$	5			<1
Bakhman et al. (30)	Cu_2O	2		0.75-1.6	<1
Shidlovskii et al. (79)	Cu_2O	5		1.2 -1.25	<1
	CuO	5		1.2 -1.25	<1
	$MnCO_3$	5		1.2 -1.25	<1
	$CuCO_3$	5	100	1.. -1.25	<1
	$MnCl_2, 4H_2O$	5	100	1.. -1.25	<1
	Co_2O_3	5	100	... -1.25	<1
	ZnO	5	100	1.. -1.25	<1
Boggs et al. (14)	MnO_4^-	0.03		1.95	115

[a] Unless specified, the ambient temperature is the room temperature.

One qualitative explanation of the role of catalysts is given by Friedman et al. (24). These authors suggested that catalysts have a dual counteracting effect on deflagration and act as follows: Catalysts increase the heat flux back to the surface by catalyzing the exothermic reaction. On the other hand, they increase the radiative heat loss from the burning surface by increasing the emissivity of AP. At low concentrations of catalyst, the increase in the heat loss is dominant and therefore the net heat flux to the surface decreases. This makes deflagration at low pressures more difficult and raises the lower pressure limit. At higher concentration of catalyst the catalyzing of the exothermic reaction outweighs the heat loss effect and results in decreasing the lower pressure limit. This explanation with the basic assumption that the radiative heat loss is the main reason for lower pressure limit was also accepted and suggested by some other investigators (55).

As a support to this model Levy and Friedman (50) reported that the addition of copper chromite to AP decreased the minimum auxiliary radiative flux necessary to maintain deflagration below the lower pressure limit. This was attributed to the increase in the absorptivity of the surface and therefore absorption of a larger fraction of the incident flux.

A completely different explanation of the effect of catalysts was suggested by Sohn (82). He developed

a model in which the surface was assumed to be covered
by a thin liquid (or frothy) layer with the exothermic
reaction taking place in gas columns passing through
this liquid zone. The heat loss from the gas columns
to the liquid walls was considered as the main reason
for extinction at the lower pressure limit. In this
model the characteristic size of these columns determines
the values of the lower pressure limit. Sohn proposed
that the catalysts change the lower pressure limit
probably by changing the surface structure and there-
fore the size of this characteristic dimension.

Even though there has been extensive research on
many aspects of the deflagration of AP, the effect of
catalysts on the pressure limits has not been systema-
tically investigated before. For this reason the present
study can be very useful for developing a model in order
to understand better the combustion of propellants.

EXPERIMENTAL METHOD

The AP used in this study was reagent grade from
Pennsalt Chemical Corporation and was recrystallized
twice for purification. A spectrochemical method with
the detection sensitivity of 100 ppm was used to detect
possible remaining impurities in the recrystallized
sample. Fe, Ca, Al, Mg, Si, Mn, Ti, Ni and Na were
looked for and were not detected. However, around
1000 ppm of potassium was detected in this sample, which

was almost twice the amount found in the as-received material. This is evidence that potassium becomes concentrated in the solid phase upon successive recrystallization. Further purification for removal of K was not necessary in these studies because the present level of K-content is shown to have negligible effect on the deflagration limit of AP (91).

The catalysts used were copper chromite ($CuCr_2O_4$, Cu-100 by Alfa Inorganic Inc.), potassium permanganate ($KMnO_4$, reagent grade by Mallinckrodt Chemical Works), cupric oxide (CuO, reagent grade by Matheson Coleman & Bell), and ferric oxide (Fe_2O_3, reagent grade by Allied Chemical).

In mechanically mixed samples, the particle size of copper chromite, Fe_2O_3 and CuO was less than 20 microns and that of $KMnO_4$ was 43-88 or 88-175 microns. AP had a particle size of 88-175 microns.

Catalysts were thoroughly mixed with AP until a uniform mixture was obtained. Uniformity of the mixture was judged by inspecting the powder under a microscope with a magnification of 15. With copper chromite, CuO and Fe_2O_3, due to the very small size of the catalyst particles, AP particles were almost covered by a fine layer of catalyst and the catalyst distribution in the bulk mixture was very uniform.

Co-crystallized samples were also prepared with $KMnO_4$. Being isomorphic with AP, potassium permanganate can be isomorphically substituted in the lattice of AP crystals. This results in a distribution of catalyst at the molecular level. For co-crystallization, a solution of potassium permanganate was added to a saturated solution of AP. The mixture was then thoroughly mixed and cooled gradually.

The concentration of $KMnO_4$ in co-crystallized samples was measured colorimetrically. This concentration was always close but a little higher than the concentration of $KMnO_4$ in the initial mother-solution. This shows the tendency of $KMnO_4$ to concentrate preferentially in the solid phase during co-crystallization.

Analytical tests showed that the concentration of manganese oxide in the co-crystallized samples was negligible. Therefore $KMnO_4$ basically remained unchanged during crystallization.

The co-crystallized samples were then ground and sieved. The fraction with particle size 88-175 microns was used in this study.

Pellets were pressed in a floating die under a pressure of 120,000 psi. Using this die, it was possible to press polycrystalline pellets of pure AP to within 1% of the density of single crystals.

Samples were ignited in a combustion chamber under N_2 pressure. An electrically-heated chromel wire was used for ignition. The ignition flux was found to be sufficient to partially burn the pellets at pressures below the lower pressure limit or above the upper pressure limit. This is important in obtaining an intrinsic pressure limit which of course must be independent of ignition technique and the strength of the ignition stimulus. A detailed description of the apparatus is given in Appendix B.

EXPERIMENTAL RESULTS

The change in the pressure limits of deflagration of AP with the concentration of four catalysts ($KMnO_4$, copper chromite, Fe_2O_3, and CuO) was studied. The results are shown in Figures II-1, II-2, II-3, II-4, and II-5. At each concentration the pressure limit is simply the boundary between the data points corresponding to the burning and non-burning conditions. To show the range of tested pressures and the accuracy of the pressure-limit determination, all the experimental runs are represented on these graphs.

Copper chromite, Fe_2O_3 and CuO (all mechanically mixed with AP) increase the lower pressure limit when present at small concentrations and decrease it at large concentrations. It is intriguing that all these

Figure II-1. The pressure limits of ammonium perchlorate with various concentrations of $KMnO_4$ (isomorphically co-crystallized with AP).

Figure II-2. The pressure limits of ammonium perchlorate with various concentrations of $KMnO_4$ [mechanically mixed samples, AP $(88-175\mu)$ + $KMnO_4$ $(88-175\mu)$].

Figure II-3. The lower pressure limit of ammonium perchlorate with various concentrations of copper chromite [mechanically mixed samples, AP (88-175μ) + cc (<20μ)].

Figure II-4. The lower pressure limit of ammonium perchlorate with various concentrations of Fe_2O_3 [mechanically mixed samples, AP (88-175µ) + Fe_2O_3 (<20µ)].
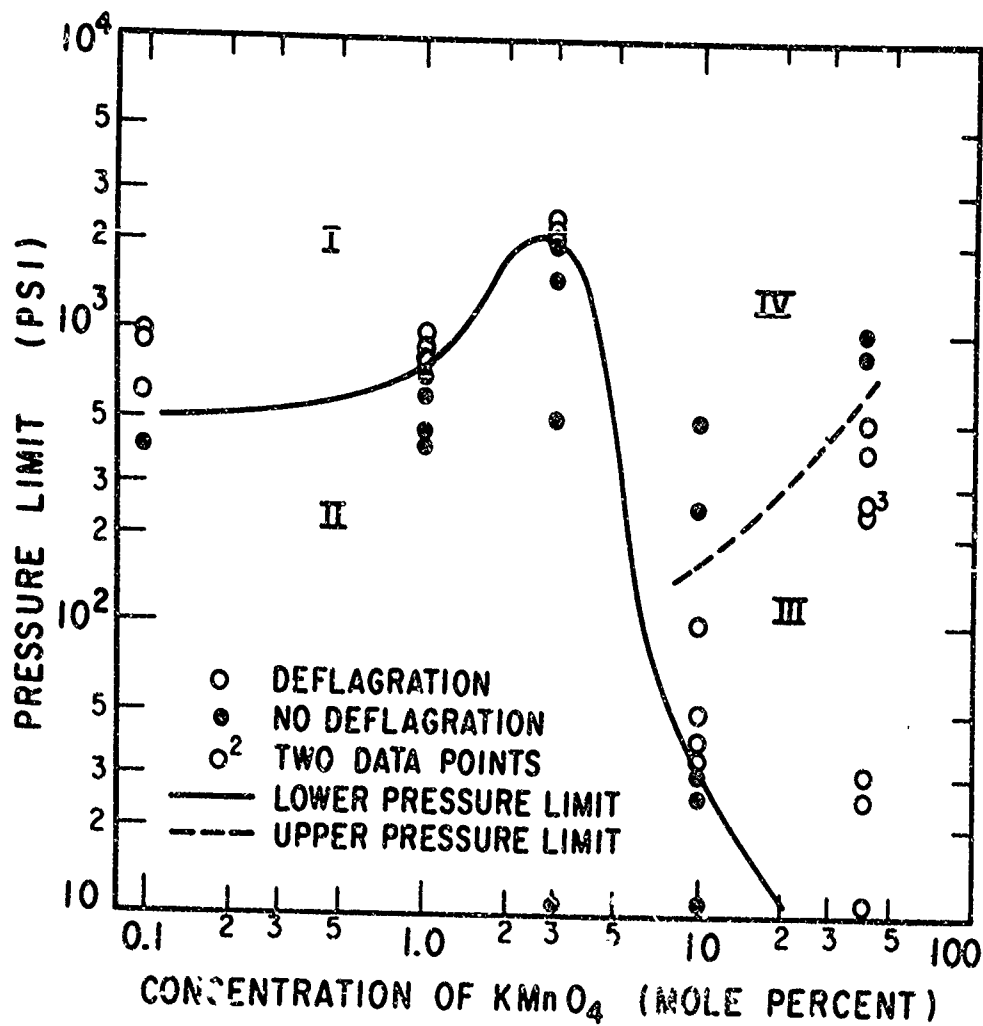
Figure II-5. The lower pressure limit of ammonium perchlorate with various concentrations of CuO [mechanically mixed samples, AP (88-175μ) + CuO (<20μ)].

catalysts cause a maximum increase in the lower pressure limit at a concentration of about 0.1 mole-%.

Potassium permanganate, both mechanically mixed and co-crystallized with AP, changed the lower pressure limit in a quantitatively similar way. However, at large concentration, $KMnO_4$ caused an upper pressure limit. This limit is shown by dotted lines in Figures II-1 and II-2. Deflagration could not be maintained at conditions corresponding to the region IV on these figures.

No upper pressure limit was observed when other catalysts were used or when $KMnO_4$ was present in small concentrations. However, these observations do not preclude the existence of an upper pressure limit at pressures higher than tested. Moreover, the boundary between the regions I and IV in Figures II-1 and II-2 cannot be definitely specified with the present data. These points should be clarified by further experiments, at higher pressures. This was not done in the present work due to the experimental difficulties and limitations.

In region III, the burning range between the lower pressure limit and the upper pressure limit narrowed as the concentration of catalyst decreased. Under conditions where the upper pressure limit and the lower pressure limit are very close to each other, the burning was difficult to maintain and any fluctuation in pressure could result in extinction of the combustion.

The present data should not be extrapolated to cases with very high concentration of catalysts. It is expected that at very high concentration the deflagration would become impossible, because the AP particles are not close enough to each other to sustain deflagration by successive ignition of particles.

To investigate the effect of catalyst distribution, the lower pressure limit was found for samples having the same composition but different catalyst particle size. The results are shown in Figure II-6. It is interesting to note that at the catalyst concentration of 0.1 mole-% the lower pressure limit almost doubles when the particle size changes from 175-88 to 88-43 microns and increases by a factor of 6 when catalyst is isomorphically substituted in the AP lattice structure.

DISCUSSION

During the deflagration of AP a number of physical and chemical changes occur. The process begins with endothermic changes which produce intermediate gaseou; products and ends with exothermic reactions which produce the final products. Usual models consider the gasification process an endothermic step and subsequent gas-phase combustion process an exothermic step. However, some authors have considered exothermic reactions in the condensed phase, too (18,29).

Figure II-6. The variation of the lower pressure limit of ammonium perchlorate with the particle size of $KMnO_4$ catalyst.

In steady deflagration, heat from the exothermic reactions is fed back to the condensed phase to maintain the endothermic steps. A part of the heat is also lost by different mechanisms of heat transfer to the surroundings and is not transferred back to the surface. This heat loss is usually assumed to become important close to the pressure limit and is considered by some to be the cause of extinction.

Catalysts probably affect most of these combustion steps, i.e., the endothermic and exothermic reactions and the heat losses. The maximum in the pressure limit on Figures II-1 to II-5 might be caused by the interaction of two effects of catalysts, and any acceptable deflagration model should have the capacity to explain the dual effect of catalysts.

Some investigators have argued that catalysts at low concentrations increase the lower pressure limit by increasing the emissivity of the burning surface and therefore increasing the radiative heat loss. It is difficult to support this argument quantitatively. For example, according to Levy and Friedman (50), copper chromite at 0.1 mole-% increases the emissivity of AP by roughly 50%. However, Figure II-3 shows that at this concentration it increases the lower pressure limit by a factor of 10. It seems unlikely that the effect of a tenfold increase in the rate of the gas-phase reactions due to the increase in pressure (100-fold for second-order reaction and even larger increase due to the effect

of catalyst) could be offset by the increase in radiative heat loss.

The existence of an upper pressure limit at high concentrations of $KMnO_4$ is an intriguing observation. Since such an upper pressure limit was not observed for other tested catalysts, it could be due to some characteristic of $KMnO_4$. One characteristic of $KMnO_4$, which was observed by analytical tests on the catalyst residues, is that it decomposed during combustion while the other catalysts almost remained chemically unchanged. Moreover, when quenched at high pressures, samples containing large quantities of $KMnO_4$ were covered with a layer of accumulated catalyst residue in the form of a fused mass. It is postulated that at high pressures where the surface temperature is high, the catalyst residue melts on the surface. At high concentrations of catalyst where this fused residue is large enough to cover the burning surface completely, deflagration is not possible. This point should be further investigated.

The pressure limit for the deflagration of pure AP is found to be practically independent of the solid particle-size provided that the pellets are tightly pressed. In the present study, pellets with a density within 1% of the density of single crystals of AP (1.95 gm/cm^3) were obtained by a special vacuum pelletizing method. These pellets had the same pressure limit as single crystals regardless of the particle size of the powder used. This observation is in agreement with

the results reported by Boggs et al. (14) regarding the melting of AP before gasification and the similarity between the surface patterns of the quenched pressed pellets and quenched single crystals. Apparently the grain structure of the solid is covered by the molten layer on the surface and therefore does not affect the combustion zone. However, if the pellets are not packed tightly enough and the size of the void spaces between the particles is comparable to the thickness of this molten zone, then the solid structure will affect the pressure limit.

In combustion of a mixture of AP and a catalyst, the distribution of the catalyst in the solid phase is very important and strongly affects the deflagration characteristics. Distribution is a general term which includes factors like size, shape and randomness of dispersion of particles. If we assume that the catalyst particles are spherical and are randomly distributed in the AP-matrix, then the particle size is the main measure of distribution.

The present results show that the catalyst becomes much more effective when its particle size decreases. This can be se   rom Figure II-6 and also from the striking difference between the results in Figure II-1 and Figure II-2. Even though the curves corresponding to the mixed and the co-crystallized $KMnO_4$-AP samples are similar qualitatively, there is a considerable difference bewteen the effectiveness of the catalyst in

each case. For example, the catalyst concentration corresponding to a lower pressure limit of 1000 psi is 1.4 mole-% for a mixed sample and only 0.0121 mole-% for a co-crystallized one (different by almost a factor of 70).

At this stage it is difficult to pinpoint specifically the reason for such differences caused by the distribution of catalyst, because the location of action and the mechanism by which the catalysts change the deflagration process are not clearly known. However, one can speculate how catalyst size could affect kinetic parameters. For example, the surface area per unit mass of catalyst, which is a direct measure of concentration of active sites, is inversely proportional to the radius of particles. Also the accessibility of active sites to the reactant molecules increases with the decrease in particle size. It can be shown that the average distance between the catalyst particles is proportional to their radius.* Therefore, decreasing the size of the

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*The number of catalyst particles per unit solid volume, N_v, is equal to $v/(\frac{4}{3} \pi r^3)$, where r is the average radius of the catalyst particles and v is the volume fraction of the catalyst in the solid mixture. The number of particles crossing the unit length of a random straight line, N_ℓ, is equal to $\pi r^2 N_v$. Therefore, the average distance between the catalyst particles is $\overline{\ell} = 1/N_\ell$, so

$$\overline{\ell} \propto \frac{4r}{3v}$$

catalyst particles results in a shorter diffusion path
for the reactant molecules moving towards the sites.
This increases the probability that the reactant molecules
find catalytic sites during their residence time in the
reaction zone.

It is important to note that the gas-phase reactions
are catalyzed by both the catalyst particles dispersed
in the gas phase and the ones partially exposed but not
detached from the condensed phase. The particles of
the second type are particularly important in most cases
due to the fact that their size is usually comparable
to the thickness of the gas-phase combustion zone. How-
ever, in both cases the size and the distance of separation
of particles affect the catalyst effectiveness.

CHAPTER III

THE EFFECT OF CATALYSTS ON THE DEFLAGRATION RATE

OF AMMONIUM PERCHLORATE

INTRODUCTION

The burning velocity is the most widely studied parameter in the deflagraion of AP. This velocity depends upon the pressure, the initial solid temperature, and the concentration of certain catalytically active additives and impurities mixed with AP.

The dependence of the burning rate on pressure and the initial solid temperature has been extensively studied and the experimental results have been to a limited extent explained by some theoretical models. However, as far as the effect of catalysts is concerned, there is very little systematic and consistent experimental work and there is no acceptable model which can explain the existing data quantitatively.

Friedman et al. (24) studied the effects of 3 wt-% copper chromite (Harshaw Chemical Co., Cu-0202, 85 wt-% CuO and 15 wt-% Cr_2O_3), CuO, Cr_2O_3, Fe_2O_3, MnO_2 and $NaMnO_4 \cdot 3H_2O$ on the deflagration of AP in the pressure range 40-340 atm. The catalyst activity was found to be a strong function of pressure. These catalysts all increased the burning rate at high pressures. Moreover, their catalytic effect increased with increase in pressure. Other additives Fe_2O_3, MnO_2 and $NaMnO_4 \cdot 3H_2O$ decreased the burning rate at low pressures but increased

it at higher pressures. The greatest increase in the deflagration rate was produced by copper chromite. This catalyst increased the burning rate in the whole pressure range. Ferric oxide (Fe_2O_3) was found to be a better catalyst for deflagration than MnO_2, even though MnO_2 is known to be a much stronger catalyst in the low-temperature decomposition of AP. This shows that the order of activity of catalysts in thermal decomposition is not necessarily the same as the order found in deflagration. These results support the contention that the results of thermal decomposition of AP should not be extrapolated and used for deflagration studies.

Friedman et al. (24) also studied the effect of concentration of copper chromite on the burning rate. It was found that copper chromite from 0.1 to 5 wt-% either augmented the deflagration rate or completely prevented burning, depending on the catalyst concentration and the pressure. However, unlike many other catalysts, it never produced a finite burning rate below that of pure AP.

Glazkova (43) studied the effect of 5 wt-% potassium dichromate and chromium oxide on the combustion of AP at pressures up to 1000 atm. The dichromate catalyzed the deflagration of AP at pressures above 30 atm. The slope of the burning rate vs. pressure curve in this case was greater than that for pure AP. Chromium oxide had a similar effect up to 100 atm, but it became less effective

at pressures above 100 atm and finally decreased the burning rate at pressures higher than 500 atm.

Boggs et al. (14) studied the deflagration of AP which was isomorphously doped with K^+, $Cr_2O_7^{-2}$ and MnO_4^-. In addition to the burning rate measurements, they investigated the change in the structure of the burning surface due to the presence of additives. This was done by observing the quenched sample under a scanning electron microscope (SEM).

In the above studies, the concentration of K^+ was changed from 0.05 wt-% to 0.8 wt-%. K^+ caused a significant change in the burning rate especially in the range 2000-7000 psi where the burning rate of pure AP goes through a minimum. It was found that K^+ preserves the general shape of the burning rate isotherm, but shifts the minimum in the burning rate to lower pressures. The SEM photographs showed the presence of a thicker layer of liquid on the burning surface of these samples.

In the same studies, the effect of $Cr_2O_7^{-2}$ (from 0.0014 to 0.015 wt-%) and MnO_4^- (0.03 wt-%) was investigated. Similar to K^+, these additives caused the greatest change in the burning rate at pressures above 2000 psi. MnO_4^- increased the burning rate at all pressures tested. For unknown reasons, the samples containing 0.0083 wt-% and 0.015 wt-% $Cr_2O_7^{-2}$ did not sustain deflagration at certain intermediate pressure intervals.

There have been some studies on the effect of catalysts on the deflagration of composite propellants.

Kuratani (48) measured the burning rate of an AP propel-
lant containing 15% of a polyester fuel and 1% of some
catalysts. The observed order of the catalysts effec-
tiveness was MgO $\sim$ Cu$_2$O >> CuCl > CuO > copper chromite
(cc) $\sim$ ZnO $\sim$ Co$_2$O$_3$ $\sim$ Cr$_2$O$_3$ > V$_2$O$_5$ > Fe$_2$O$_3$ $\sim$ no catalyst.
It is interesting to note that the order of the effec-
tiveness of different catalysts in the deflagration of
composite propellants and pure AP is not the same.
For example, MgO, cc, Cr$_2$O$_3$ and Fe$_2$O$_3$ catalyze the
burning of pure AP in the following order: cc > Fe$_2$O$_3$ >
MgO > Cr$_2$O$_3$; while, according to Kuratan: (48), their
effectiveness on the deflagration of AP + polyester fuel
is MgO > cc > Cr$_2$O$_3$ > Fe$_2$O$_3$. Surprisingly, MgO, which
is much weaker than cc in catalyzing the deflagration of
pure AP, is a much stronger catalyst in the burning of
composite propellant.

The effect of catalysts on the distribution of final
products of deflagration of AP has been subject to
numerous studies. Levy et al. (50) and Arden et al. (2)
examined the gaseous products of AP combustion and found
that N$_2$O yield dropped greatly on the addition of copper
chromite. Arden et al. (2) similarly observed that
copper chromite reduced the amount of NO present in the
gas phase. Based on these observations, it seems that
copper chromite and most other catalysts enhance the
reactions which reduce nitrogen oxides to N$_2$.

The mechanism of the reactions and where the catalyst action takes place are not yet clearly known. The strong dependence of catalytic effectiveness on pressure indicates that the catalysts mainly act in the gas phase. The reason that the catalysts become more effective at high pressures is that more gas-phase collisions between the catalyst and the gaseous reactants would occur in the region close to the surface. This increases the rate of heat transfer to the solid and enhances the deflagration rate. Pittman (60) argued that the depth to which high temperature extends below the burning surface decreases as the pressure increases. Therefore the residence time alloted for probable reactions occurring beneath the surface sharply decreases as the pressure increases. This means that if the catalysts were effective below the surface, their effect would decrease as P increased.

Pittman (60) made the following observations regarding the location of action of catalysts in the deflagration of composite propellants:

a) propellants containing AP coated with a catalyst burned at the same rate as the propellants in which the same amount of catalyst was mixed into the binder.

b) co-precipitation of catalyst with AP did not increase the effectiveness of the catalyst compared with mixing the catalyst with the binder mechanically.

Based on these observations they concluded that the subsurface reactions were insignificant and suggested that catalysts were mainly active in the gas-phase during the deflagration of composite propellants. However, heterogeneous surface reactions were not excluded from the term "gas-phase". It should be noted that these observations only showed that the way catalyst particles are embedded in the composite propellants is not important; however, they did not rule out the importance of the catalyst particle size.

In summary, very little is understood and can be generalized about the way catalysts change the burning rate of AP. This is partly due to the complexity of the problem and partly due to the scarcity of systematic experiments in this field. The data obtained by different investigators can hardly be compared due to the significant differences in the experimental conditions. The particle size of AP and the catalysts, the density of the pellets, the method of preparation of the samples, the nature of the fuel in case of composite propellants and many other factors usually change from one to another set of existing data. Considering the importance of all these factors in determining the deflagration rate, there is a need for a systematic research in which each of these factors is isolated and its role is investigated separately.

EXPERIMENTAL NOTES

The preparation of the samples and the experimental procedure were similar to those explained in Chapter II. The burning rates were obtained by the analysis of the movies in each run.

In the deflagration of pure AP, the burning surface usually remains flat and regresses at a fairly uniform rate. The burning of the samples containing catalysts, however, is normally less uniform and the rates are less reproducible. It was observed that the samples containing $KMnO_4$ especially suffered an erratic burning accompanied by some changes in the shape and the angle of the burning surface and sometimes cracking of the samples. Occasionally the catalyst residue, accumulated on the burning surface, would roll down the side of the pellet and sometimes would initiate a lateral burning. Copper chromite and Fe_2O_3, however, caused less non-uniformity in the burning of AP.

Samples of AP containing $KMnO_4$ had a much longer ignition delay compared to the others. This long ignition time would cause some preheating of the upper part of the sample and would obviously change the burning rate of that part of the pellet. As shown in Figure III-1, the burning rate of such samples decreased as the burning proceeded and then remained almost constant for that

Figure III-1. Variation of the burning rate along the pellets of ammonium perchlorate.

section of the pellet which was not preheated significantly. This observation indicates that any kind of averaging for obtaining an overall burning rate for the whole pellet would give erroneous results in such cases. Therefore, it is important to consider the change in the burning rate along the pellet in each run and exclude the portion which has been preheated.

Accumulation of the catalyst residue on the burning surface was an important cause of the nonuniform burning of some samples. Sometimes excessive accumulation made rate determination very difficult by covering and blocking the view of the burning surface in the movies. It is also likely that the accumulation of catalysts might have introduced some errors in the burning-rate results. The importance of such effects should be further investigated.

At small concentrations, the catalyst particles are separated from each other in a matrix of AP and can be carried away by the convective flow of the gaseous products provided that the drag force on them is larger than their weight. Smaller particles can be carried away more easily because

$$\text{drag force} \propto \text{(particle size)}$$
$$\text{gravity force} \propto \text{(particle size)}^3$$

which shows that at small values of particle size the drag force becomes dominant.

At large concentrations, where catalyst particles stick to each other, the drag force may not be large enough to break and separate them; thus, a residue remains on the surface. This was verified experimentally; at concentrations higher than about 10 mole-%, a porous residue of catalyst was left behind which had the same shape and size as the original pellet. This showed that AP particles successively burned witnout displacing the catalyst structure in the pellet.

In cases where the catalyst was melted by the heat in the combustion zone, the accumulation was observed even at small concentrations and fine dispersion of catalyst. For example, $KMnO_4$ left a residue which looked like a fused mass. In this case the accumulation was observed at concentrations as low as 0.1 mole-% even when $KMnO_4$ was distributed in the molecular level. At concentrations above 10 mole-%, the residue was mostly porous, probably because the heat was not enough to fuse the relatively large mass of the residue.

The analytical tests on the catalyst residues showed that ferric oxide and cupric oxide remained unchanged during combustion. Only less than 1 wt-% of the oxides was converted to chlorides. On the contrary, almost all of $KMnO_4$ was decomposed; the residue was insoluble in water and contained 4-5 wt-% potassium and 35-40 wt-% manganese; the rest was mainly oxygen and water.

Obtaining reliable and reproducible data on the burning rate of AP + catalyst involves difficulties which are not observed in the experiments with pure AP. As was explained, accumulation of catalyst and preheating of a section of the pellet make the burning rate nonuniform along the pellet; therefore, an overall burning-rate measurement is not satisfactory. Moreover, cracking and separation of unburned pieces from the pellets sometimes cause an apparently fast burning. This can be misleading if the detail of the burning is not observed. In the present study the method of high-speed photography was used for the burning-rate measurements in order to be able to observe and consider such anomalies during the burning.

DISCUSSION OF RESULTS

The effect of $KMnO_4$ on the burning rate of AP was investigated; the results are shown in Figure III-2. It is observed that $KMnO_4$ decreases the burning rate slightly in most cases, especially when it is co-crystallized with AP. This inhibition of the burning rate can be partly due to the accumulation of the residue which hinders the heat transfer to the condensed phase.

The effect of copper chromite on the burning rate of AP has been partly studied by Friedman et al. (24). Some data were obtained in this work. As shown in

Figure III-2. Burning rate of ammonium perchlorate with various concentrations of $KMnO_4$.

Figure III-3, copper chromite increases the burning rate significantly at all pressures. It is interesting to note that, compared to $KMnO_4$, copper chromite is a much stronger catalyst for deflagration and a much weaker catalyst for decomposition.

The effectiveness of the catalysts is a strong function of both the concentration of the catalysts and the pressure. Usually, the effectiveness increases with the increase in pressure. The greatest change in the burning rate by most catalysts is in the range above 2000 psi where the burning rate of pure AP goes through a minimum. Even a small amount of a catalyst is usually very effective in this pressure range. This supports the idea that the scattering of the data on the burning rate of pure AP is mainly due to the presence of impurities in different samples (72).

The strong effect of catalysts above 2000 psi cannot be explained at this stage mainly because the reason for the drop in the burning rate of pure AP is not understood. There has been speculation that the drop in the burning rate is due to the convective heat losses. This is unlikely because, first of all, convective heat losses increase gradually and not sharply with the increase in pressure, and secondly, the drop in the burning rate is very sensitive to traces of catalysts while convective heat losses do not change significantly with addition of catalysts. It is more likely that the drop in the burning rate of pure AP around 2000 psi is due to

Figure III-3. Burning rate of ammonium perchlorate
with various concentrations of copper chromite.

some changes in the surface structure and the physical
nature of the so-called "frothy" reaction zone. If so,
most additives c·nge the burning rate in this pressure
range mainly by changing the structure of the frothy
zone rather than by catalyzing the combustion reactions.
A support for this idea is the strong effect of potassium.
There are indications that K^+ changes the amount of frothy
melt on the surface significantly (14) even though its
catalytic effect on the combustion reactions is probably
negligible.

A very intriguing observation is the value of the
burning rate of samples at pressures close to the lower
pressure limit. Figure III-4 shows these values extra-
polated from the burning rate data and plotted against
the corresponding pressure limit. Surprisingly, these
limiting rates are very close to the burning rates of
pure AP shown by the solid line on Figure III-4. This
is an indication that the effect of catalysts on the
burning rate diminishes close to the pressure limit; or,
in other words, at pressures close to the lower pressure
limit the burning rate is only a function of pressure
and not the concentration and the nature of the additives.
This is surprising especially because the value of the
lower pressure limit is very sensitive to the presence
of catalysts. At this stage, it is not clear whether
this conclusion is general or is only valid for some
catalysts. However, further investigation of this
observation could be very interesting and valuable.

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Figure III-4. Burning rate of ammonium perchlorate + catalyst at pressures very close to the lower pressure limit.

APPENDIX A

SPECIFICATIONS OF "AS RECEIVED"

AMMONIUM PERCHLORATE

The following specifications were reported for ammonium perchlorate by Pennsalt Chemical Corporation:

Reagent grade

Minimum ammonium perchlorate	99.5%

Maximum impurities specified were :

Chlorates as NH_4ClO_3	0.01
Chlorides as NH_4Cl	0.10
Bromates as NH_4BrO_3	0.001
Water insoluble	0.00
Sulfates as $(NH_4)_2SO_4$	0.00
Non-alkali metals as oxides	0.00
Sodium and potassium	0.05%

APPENDIX B

EXPERIMENTAL APPARATUS FOR THE STUDY OF

THE COMBUSTION OF AMMONIUM PERCHLORATE

PELLETIZING APPARATUS

A cylindrical vacuum die was designed and made
from E9310 Carburized steel. A schematic diagram of
the die is shown in Figure B-1. This die was a floating
type and therefore could provide a better distribution
of the pelletizing pressure than a die having a fixed
plunger. It was designed for the maximum safe pel-
letizing pressure of 150,000 psi. Pellets pressed in
this die had a diameter of 0.95 cm and a length of
1-2 cm. The AP pellets pressed in this die had a
density within 1% of the density of the single crystals.
Air between the powder particles could be pumped out
through a vacuum tube. Three O-rings, placed in the
special slots of the upper and the lower plungers, pro-
vided seals. A minimum pressure of 50 microns could
be maintained by this set-up.

COMBUSTION SYSTEM

A schematic diagram of the combustion system is
shown in Figure B-2. The apparatus consisted of three
major parts: the combustion chamber, the photographic
system and the control center. Figures B-3 and B-4
show the first two parts.

A = Cap for the upper plunger
B = Upper plunger
C = Die body
D = O-rings
E = Vacuum tube
F = AP powder
G = Lower plunger (base)

Figure B-1.   Schematic diagram of pelletizing die.

Figure B-2. Schematic diagram of apparatus.

Figure B-3. Combustion chamber and high-speed movie camera.

Figure B-4.   Combustion chamber, high-speed movie
camera, and titling board.

(a) <u>Combustion Chamber</u>: The combustion chamber
was a stainless-steel cylinder. Both ends of this
cylinder were threaded and were fitted with stainless-
steel end plates, O-rings and threaded aluminum com-
pression caps. Two quartz windows, mounted in two
cylinders perpendicular to the chamber, were provided
for photographing the combustion of the pellets. The
combustion chamber was mounted on a support fastened
to the base of a safety shield. To minimize the pressure
fluctuations during the combustion, an auxiliary
stainless-steel surge tank was attached to the main
combustion chamber. This system was designed for about
25,000 psi and was hydrostatically tested at 9600 psi
to insure safe operation up to 5000 psi.

Figure B-5 shows the end plate and the assembly
attached to it. A Chromel electric wire was used to
ignite the pellets. A photoresistor or photovoltaic
cell was used to monitor the burning and to indicate
the beginning and the end of the burning of the samples.
Alumel-Chromel thermocouples were used to measure the
temperature of the pellet and the inside of the chamber.
The pressure of the chamber was measured by both a
high-pressure gauge and a pressure transducer.

To provide a clear view of the burning pellet, the
combustion products were removed by maintaining a con-
stant flow of N_2 around the pellet. The inlet and the
outlet for this flow were two funnel-shaped channels
below and above the pellet. The outlet gases were passed

Figure B-5. "End plate" assembly with the smoke-removal device.

through a high-pressure filter-trap where most soluble
gases were absorbed in water. The removal of some
corrosive gases such as HCl in this filter reduced the
problem of corrosion in the down-stream equipment.
The flow of N_2 in the smoke-removal device was regulated
by a combination of a metering valve and a rotameter.
The removal of gaseous products was especially necessary
during the runs with catalysts, because the gaseous
products were very dark and dense in the pictures due
to the fine dispersion of catalyst particles in the gas
phase. Tests with different flow rate of N_2 showed
that this smoke-removal technique did not interfere
with the burning surface and did not change the defla-
gration characteristics.

(b) Photographic System: A high-speed motion
picture camera was used to photograph the burning of
the pellets. As shown in Figures B-3 and B-4, the camera
was mounted on a rotary table allowing pictures to be
taken of the pellet inside the chamber in one position
and pictures of the title board in another position.
A timing-light generator was used to record the intervals
of 1/10 second on the edge of the film.

(c) Control Center: The control center mainly
consisted of two variacs for changing the speed of the
camera and the voltage across the ignition wire, a
preamplifier and a two-channel oscillograph for re-
cording the outputs of the thermocouples, the pressure
transducer and the photocell.

APPENDIX C

EXPERIMENTAL DATA

Table C-1. Data on Deflagration of AP Co-Crystallized with $KMnO_4$ [a]

Ambient Temperature °C	Pressure psi	Catalyst Concentration mole-%	Self-Sustained Deflagration	Burning Rate cm/sec	Run No.
18	1200	0.011	yes	0.63	100
24	1000	0.011	yes	0.67	3
24	1000	0.011	yes	0.56	4
24	1000	0.011	yes	b	5
18	900	0.011	yes	0.43	99
24	800	0.011	yes	0.56	8
24	700	0.011	yes	0.34	90
24	700	0.011	yes	b	89
24	600	0.011	no	--	88
24	500	0.011	no	--	87
24	300	0.011	no	--	6
20	3000	0.024	yes	1.10	133
18	2050	0.024	yes	0.90	101
20	1300	0.024	yes	0.75	131
18	1200	0.024	yes	b	122
20	1160	0.024	yes	0.69	132
18	1150	0.024	yes	b	125
18	1100	0.024	no	--	124
18	1000	0.024	no	--	121
18	900	0.024	no	--	123

Table C-1 continued.

Ambient Temperature °C	Pressure psi	Catalyst Concentration mole-%	Self-Sustained Deflagration	Burning Rate cm/sec	Run No.
19	3100	0.064	yes	b	116
18	2000	0.064	no	--	183
18	1000	0.064	no	--	182
17	3300	0.135	yes	0.43	92
23	3000	0.135	yes	b	13
18	2900	0.135	yes	0.40	93
17	2800	0.135	no	--	94
17	2600	0.135	no	--	91
24	2500	0.135	no	--	12
24	2000	0.135	no	--	11
24	1500	0.135	no	--	10
24	1000	0.135	no	--	9
18	3200	0.654	no	--	112
19	3100	0.654	no	--	117
18	1750	0.654	no	--	111
18	1500	0.654	no	--	110
18	1000	0.654	no	--	106
20	1000	0.654	no	--	102
20	1000	0.654	no	--	103
18	1000	0.654	no	--	126
18	500	0.654	no	--	108
18	200	0.654	no	--	107
20	150	0.654	no	--	127
20	130	0.654	no	--	128

Table C-1 continued.

Ambient Temperature °C	Pressure psi	Catalyst Concentration mole-%	Self-Sustained Deflagration	Burning Rate cm/sec	Run No.
20	120	0.654	no	--	130
20	110	0.654	no	--	129
19	100	0.654	no	--	118
20	70	0.654	yes	b	156
21	50	0.654	yes	b	160
20	25	0.654	yes	b	155
20	15	0.654	no	--	157
20	1000	1.32	no	--	151
20	500	1.32	no	--	14^
20	200	1.32	no	--	149
20	150	1.32	no	--	150
20	150	1.32	yes	b	152
20	100	1.32	yes	0.04	146
20	100	1.32	yes	b	143
20	50	1.32	yes	0.04	147
21	50	1.32	yes	0.05	154
20	25	1.32	yes	b	144
20	1	1.32	no	--	145
20	1500	2.52	no	--	170
20	1000	2.52	no	--	168
20	500	2.52	no	--	179
20	300	2.52	no	--	180
20	200	2.52	yes	b	134
20	100	2.52	yes	b	135

Table C-1 continued.

Ambient Temperature °C	Pressure psi	Catalyst Concentration mole-%	Self-Sustained Deflagration	Burning Rate cm/sec	Run No.
20	100	2.52	yes	b	139
20	30	2.52	yes	b	137
20	30	2.52	yes	b	138
19	20	2.52	yes	b	140
19	10	2.52	yes	b	141
21	10	2.52	no	--	181
20	1	2.52	no	--	136
20	1900	10.0	yes	0.44	115
20	1500	10.0	yes	0.35	114
20	1000	10.0	yes	b	113
23	500	10.0	yes	0.32	
23	260	10.0	yes	b	80
22	250	10.0	yes	b	78
23	240	10.0	yes	b	79
22	100	10.0	yes	b	73
21	100	10.0	yes	0.24	86
22	50	10.0	yes	b	76
22	20	10.0	yes	b	74
22	15	10.0	yes	b	223
21	10	10.0	yes	b	224

[a]Particle size of the co-crystallized powder used to press pellets = 88 - 175 μ.

[b]The burning rate was not measured.

Table C-2. Data on Deflagration of AP Mechanically
Mixed with $KMnO_4$[a]

Ambient Temperature °C	Pressure psi	Catalyst Concentration mole-%	Self-Sustained Deflagration	Burning Rate cm/sec	Run No.
23	1000	0.1	yes	1.30	1
23	1000	0.1	yes	1.40	2
21	1000	0.1	yes	b	158
20	900	0.1	yes	b	214
21	800	0.1	yes	b	159
21	600	0.1	yes	b	213
21	600	0.1	no	--	160
20	400	0.1	no	--	212
19	1000	1.0	yes	b	215
19	900	1.0	yes	b	221
19	800	1.0	yes	b	220
19	700	1.0	no	--	219
19	600	1.0	no	--	218
19	450	1.0	no	--	217
19	400	1.0	no	--	216
22	2500	3.0	yes	0.52	19
22	2300	3.0	yes	b	18
24	2250	3.0	yes	0.38	16
22	2000	3.0	no	--	17
24	1500	3.0	no	--	15
24	500	3.0	no	--	14
23	10	3.0	no	--	20

Table C-2 continued.

Ambient Temperature °C	Pressure psi	Catalyst Concentration mole-%	Self-Sustained Deflagration	Burning Rate cm/sec	Run No.
22	500	10.0	no	--	75
23	260	10.0	no	--	81
23	100	10.0	yes	0.05	72
23	60	10.0	yes	0.04	71
20	50	10.0	yes	b	67
20	40	10.0	yes	b	68
22	35	10.0	yes	b	69
22	30	10.0	no	--	70
20	25	10.0	no	--	65
20	10	10.0	no	--	66
19	1000	40.0	no	--	222
21	850	40.0	no	--	62
21	500	40.0	yes	b	61
20	400	40.0	yes	b	64
23	260	40.0	yes	b	82
21	260	40.0	yes	b	83
21	260	40.0	yes	b	84
21	250	40.0	yes	b	85
20	30	40.0	yes	b	31
20	25	40.0	yes	b	32
21	10	40.0	yes	b	60

[a]Particle size of AP and $KMnO_4$ powder used to press pellets = 88 - 175 µ.

[b]The burning rate was not measured.

Table C-3. Data on Deflagration of AP Mechanically
Mixed with Copper Chromite[a]

Ambient temperature °C	Pressure psi	Catalyst Concentration mole-%	Self-Sustained Deflagration	Burning Rate cm/sec	Run No.
20	2000	0.03	yes	b	187
20	2000	0.03	yes	b	188
20	1500	0.03	no	--	190
20	1000	0.03	no	--	189
20	3200	0.10	yes	b	194
20	2800	0.10	no	--	193
19	2500	0.10	no	--	191
19	2000	0.10	no	--	192
21	3000	0.20	yes	b	195
21	2000	0.20	no	--	197
21	1000	0.20	no	--	196
21	1000	1.0	yes	b	57
21	900	1.0	yes	0.65	58
21	800	1.0	yes	0.55	59
21	700	1.0	no	--	56
21	600	1.0	no	--	55
23	460	1.0	no	--	54
23	400	1.0	no	--	53
22	1000	3.0	yes	2.7	46
23	600	3.0	yes	0.95	47
22	500	3.0	yes	b	44

Table C-3 continued.

Ambient Temperature °C	Pressure psi	Catalyst Concentration mole-%	Self-Sustained Deflagration	Burning Rate cm/sec	Run No.
22	500	3.0	yes	0.69	48
23	400	3.0	yes	0.35	45
23	200	3.0	no	--	43
23	100	3.0	no	--	42
23	50	3.0	no	--	23
23	50	3.0	no	--	24
23	50	3.0	no	--	41
23	50	3.0	no	--	38
23	10	3.0	no	--	21
23	10	3.0	no	--	22
23	10	3.0	no	--	25
23	10	3.0	no	--	39

[a]Particle size of AP = 88 - 175 μ. Particle size of copper chromite <20 μ.

[b]The burning rate was not measured.

Table C-4. Data on Deflagration of AP Mechanically
Mixed with CuO[a]

Ambient Temperature °C	Pressure psi	Catalyst Concentration mole-%	Self-Sustained Deflagration	Run No.
20	1500	0.03	yes	199
20	700	0.03	no	198
20	600	0.03	no	200
19	3000	0.10	yes	203
19	2500	0.10	yes	204
19	2000	0.10	no	202
19	1000	0.10	no	201
19	500	0.10	no	205
19	2500	0.30	yes	207
19	2000	0.30	no	208
19	1000	0.30	no	206
20	1500	1.0	yes	209
20	800	1.0	no	211
20	600	1.0	no	210
20	80	10.0	yes	186
20	40	10.0	no	185
20	20	10.0	no	184

[a]Particle size of AP = 88 - 175 μ.   Particle size of
CuO <20 μ.

Table C-5. Data on Deflagration of AP Mechanically Mixed with Fe_2O_3[a]

Ambient Temperature °C	Pressure psi	Catalyst Concentration mole-%	Self-Sustained Deflagration	Run No.
20	1700	0.05	yes	176
20	900	0.05	no	175
20	500	0.05	no	174
20	1500	0.20	yes	169
20	1000	0.20	no	167
21	1000	1.0	yes	163
21	1000	1.0	yes	178
20	950	1.0	yes	166
21	850	1.0	no	177
20	800	1.0	no	165
20	500	1.0	no	164
20	100	1.0	no	162
17	500	10.0	yes	172
17	100	10.0	yes	173
17	25	10.0	no	171

[a]Particle size of AP = 88 - 175 μ. Particle size of Fe_2O_3 <20 μ.

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